

**EQUILIBRIUM GEOCHEMICAL MODELING OF A SEASONAL THERMAL ENERGY
STORAGE AQUIFER FIELD TEST**

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PROJECT OUTLINE I

Project Title: Advanced Analysis Methodologies (Mathematical Modeling)

Principal Investigator: C. T. Kincaid

Organization: Pacific Northwest Laboratory
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Project Goals: To develop numerical simulation technology capable of predicting the transport of a stored thermal resource within the ground-water environment.

Expand currently available ground-water models to include energy transport.

Verify the expanded models through use of available data sets (which include energy parameters).

Apply the verified models to proposed LETF sites.

Develop an energy transport model for unconfined aquifers.

Apply the unconfined model to a representative aquifer/energy storage system.

Document the models developed.

Apply data from the laboratory and field experiments to account for observed changes.

Project Status: Project was initiated in October, 1979.

Contract Number: EY-76-C-06-1830

Contract Period: October 1979 (Continuing)

Funding Level: \$170,400 (FY 1980)

Funding Source: Energy Storage Systems Division
U.S. Department of Energy

PROJECT OUTLINE II

Project Title: Advanced Analysis Methodologies (Laboratory)

Principal Investigator: J. A. Stottlemire

Organization: Pacific Northwest Laboratory
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Project Goals: To conduct laboratory investigations of well injection and water quality problems anticipated under ATES reservoir operating conditions.

Develop laboratory scale equipment capable of closely "simulating" in situ ATES mechanical and thermal loading conditions. Priorities are on effective stress, temperature, and fluid-flow conditions. Such equipment should be available to support LETF and demonstration sites.

Investigate the phenomena of time and/or temperature-dependent changes in hydraulic conductivity and bulk compressibility.

Develop a standard suite of tests applicable to each potential LETF or demonstration facility. Emphasis shall be on identifying operational and/or environmental problems and recommending mitigating techniques

Project Status: Project was initiated in October 1979.

Contract Number: EY-76-C-06-1830

Contract Period: October 1979, Continuing

Funding Level: \$105,000 (FY 1980)

Funding Source: Energy Storage Systems Division
U.S. Department of Energy

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ABSTRACT

The report summarizes a geochemical mathematical modeling study designed to investigate the well plugging problems encountered at the Auburn University experimental field tests. The results, primarily of qualitative interest, include: 1) loss of injectivity was probably due to a combination of native particulate plugging and clay swelling and dispersion, 2) fluid-fluid incompatibilities, hydrothermal reactions, and oxidation reactions were of insignificant magnitude or too slow to have contributed markedly to the plugging, and 3) the potential for and contributions from temperature-induced dissolved gas solubility reductions, capillary boundary layer viscosity increases, and microstructural deformation cannot be deconvolved from the available data.

INTRODUCTION

Since 1976, two field experiments have been conducted by Auburn University involving storage of heated waters in a shallow, confined aquifer near Mobile, Alabama (ref. 1 and 2). The first experiment involved injection of 7,570 m³ of 37°C, filtered water from an electric power plant cooling water canal. The storage aquifer is located between 40 and 62 m below the land surface. The heated canal water was stored for 37 days and then recovered with an overall thermal efficiency of 67%. The process was inhibited by significant plugging of the injection well. This has been attributed to clay and silt particles suspended in the canal water; filtering above the 5-micron range improved but did not eliminate the problem.

A second experiment, utilizing the same storage aquifer, involved a 79-day injection of 55,345 m³ of 55°C boiler heated water. The water source was an unconfined aquifer located between 25 m and 34 m below the land surface. The water was stored for 50 days and then retrieved over a 41-day period. The recovery efficiency was 65% over a temperature range of 55°C and 3°C. Ambient groundwater temperature was 20°C. Figure 1 is a schematic of this second experiment. It is important to note that the supply water was extracted from an overlying aquifer and, therefore, the system did not represent a true doublet configuration.

Clogging of the injection well again proved to be a major operational difficulty. Loss of permeability resulted in a decrease in the maximum

injection rate from $12.6 \text{ l}\cdot\text{sec}^{-1}$ (200 gpm) to $6.3 \text{ l}\cdot\text{sec}^{-1}$ (100 gpm). Plugging of the well may have been due to the water sensitive nature of the storage aquifer sediments. Montmorillonite clay in combination with low cation concentration of the supply water relative to the storage aquifer water may have resulted in swelling and dispersion of clay particles as shown conceptually in figure 2. Such water sensitivity is a documented phenomenon which lends itself to laboratory identification and field pretreatment (ref. 3, 4, 5). It is also possible that the supply aquifer water contained suspended solids and/or dissolved gases which may have contributed to the plugging.

In general, there are other potential reservoir permeability damage mechanisms including precipitation of minerals due to the mixing of incompatible groundwaters, water-rock incompatibility, increased temperatures, boundary layer viscosity anomalies (ref. 6), and microstructural deformation (ref. 7).

The primary objective of this study is to investigate fluid-fluid incompatibility, fluid-rock incompatibility, hydrothermal mineral alterations, and redox reactions with respect to potential contribution to the loss of well injectivity observed at the Auburn field experiments. This investigation was based on equilibrium chemical thermodynamic computer modeling. No laboratory and/or post-experimental field data are available for comparison, and therefore the results of this computer study are only of qualitative value.

Sediment and Groundwater Characterization

Approximate groundwater chemistry is shown in table 1. Sediment mineralogy and grain size distribution are given in tables 2 and 3.

Description of Test Cases

The objective of this study is to analyze some potential alternate causes of formation plugging at the Auburn field test. The following observations are noted:

- The shallow partially confined supply aquifer is low in ionic concentration relative to the storage aquifer, and has unknown suspended solid and dissolved gas concentrations.
- The deeper, confined, storage aquifer water is assumed to be in chemical equilibrium with the formation mineralogy at a temperature of 19.5°C .
- The supply and storage waters were increased in temperature from 19.5°C to approximately 55°C .

- Plugging occurred when the supply aquifer water was used as the working fluid.
- Plugging apparently did not occur when the storage formation water was injected back into the storage aquifer. This water was not heated however (Molz, Auburn University, personal communication).

Based on these observations and a water sensitivity test conducted at Auburn University, (Molz, personal communication), it is probable that the loss in well injectivity resulted primarily from particle plugging and clay swelling and dispersion. The montmorillonite content is less than a percent by weight; however, this is often sufficient to inhibit the flow of low salinity waters (ref. 3). Furthermore, dispersed particles in the micron and submicron range can often significantly reduce permeability (ref. 5).

Other potential reservoir damage mechanisms amenable to chemical thermodynamic modeling include:

- mineral precipitation as the working fluid temperature is increased
- mineral precipitation as oxygen is introduced to the system
- mineral precipitation due to the mixing of the potentially incompatible supply and storage formation waters
- mineral precipitation due to a chemical incompatibility between the supply water and the storage aquifer sediment and/or hydrothermal alteration products.

To study these four potential categories, several computer simulations were conducted as listed in table 4.

Data Analysis and Conclusions

For each computer simulation, the following equilibrium data were tabulated: 1) equilibrium mineralogy, 2) type and quantity of new mineral precipitates, 3) fluid temperature and pH, and 4) aqueous species concentrations. It is assumed that if minerals precipitate to any significant degree, decreased formation permeability might result.

Increasing the working fluid temperature and/or oxygen content (Eh) apparently has a negligible effect on mineral precipitation. Hematite, a ferric (iron) oxide, is the only mineral susceptible to precipitation. However, as shown in table 5, the quantity in moles per kilogram of water is rather insignificant. In addition, mixing the supply aquifer water and the storage aquifer water does not result in deleterious mineral precipitation; therefore, fluid-fluid incompatibility should be discounted as a contributing factor in the observed formation plugging at the Auburn field tests.

Alteration of the storage aquifer mineralogy was also investigated. This scenario involves interacting the heated supply water with ambient temperature groundwater and sediments in the storage aquifer. Table 6 shows the ionic concentrations in the groundwater and equilibrium mineralogy predicted by EQUILIB for four different injection water temperatures. With respect to the mineralogy at 55°C, it can be observed that EQUILIB predicts that calcite, muscovite, and kaolinite all react to some extent and that the minerals adularia and calcium montmorillonite would be formed as products. Similarly, the feldspars microcline and low-albite apparently react and zoisite is a predicted reaction product. As the injection water temperature is increased, there is a net decrease in the amount of solid material within any volume of rock equilibrated at these temperatures. To maintain a mass balance, there is an increase in the aqueous species concentration of the fluid. This might indicate that as the temperature decreases with increasing distance from the well, precipitation may occur. If the fluid is saturated with respect to certain mineral species at elevated temperature near the well, transport of the fluid to a lower temperature environment could result in precipitate formation. The consequences of such precipitation would depend, in part, on the quantity and density of the precipitate and the interstitial makeup of the sedimentary matrix. However, kinetics is an additional factor that must be considered.

Based on equilibrium predictions, it might be argued that hydrothermal mineral alteration contributed to the plugging observed at the Auburn test site. However, the computer results should be viewed with caution and considered to be qualitative only. Because of thermodynamic inconsistencies in the data base and the equilibrium assumption, results predicted by complex geochemical computer codes may not always be accurate. The assumption that the heated supply water, the storage aquifer water, and the storage aquifer mineralogy have achieved a stable equilibrium becomes quite restrictive if the temperature under consideration is as low as 55°C. Reaction rates of rock-forming minerals with aqueous solutions may be extremely slow. Hydrothermal reactions probably do not occur rapidly enough to account for the plugging observed in the first 48 hours of the Auburn experiment.

It is concluded that with the possible exception of clay swelling and dispersion, fluid-rock incompatibility was not a contributing factor in the formation damage in the Auburn tests. Furthermore, heating the supply water, introducing oxygen, and mixing the supply and storage formation waters apparently had no effect on precipitation of minerals or the creation of alteration products that could reasonably explain the formation damage. Based on the limited evidence, it is assumed that water sensitivity (clay swelling and dispersion), particulate plugging, and outgassing of dissolved gasses represent the most reasonable explanations for the loss of injectivity in this specific case. More detailed study might reveal that temperature-induced capillary boundary layer viscosity anomalies or microstructural deformation may have been contributing factors. Table 7 is a summary of the potential formation damage mechanisms and a qualitative estimate of the relative likelihood of each having occurred at the Auburn facilities.

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TABLE 1. GROUNDWATER CHEMISTRIES AS SUPPLIED BY AUBURN UNIVERSITY

Water Type	Supply Aquifer (Unconfined Aquifer)		Storage Aquifer (Confined Aquifer)	
	mg/l		(mg/l)	
	Sample 1	Sample 2	Sample 1	Sample 2
Na	3.40	0.60	7.60	11.10
Ca	0.33	0.21	0.05	0.38
Fe	0.07	0.07	0.06	0.05
Si	6.30	9.10	10.40	9.70
CaCO ₃	3.80	3.80	176.00	176.00
pH	7.19	7.19	7.38	7.38
Temperature	19.5°C	19.5°C	19.5°C	19.5°C

TABLE 2. INITIAL SAMPLE MINERALOGY BASED ON OPTICAL PETROGRAPHY AND X-RAY DIFFRACTION

Mineral	Composition	Concentration (Vol%)
Calcite	CaCO ₃	3.7
Quartz	SiO ₂	76.5
Hematite	Fe ₂ O ₃	2.5
Muscovite	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	1.3
Kaolinite	Al ₄ Si ₄ O ₁₀ (OH) ₈	2.8
Alkali Feldspar	(K,Na)AlSi ₃ O ₈	8.3
Plagioclase Feldspar	NaAlSi ₃ O ₈ - CaAl ₂ Si ₂ O ₈	4.5
Montmorillonite	(1/2Ca,Na,K) _{0.7} (Al,Mg,Fe) ₄ (Al,Si) ₈ O ₂₀ (OH) ₄ • nH ₂ O	0.4

TABLE 3. GRAIN SIZE DISTRIBUTION FROM SIEVE ANALYSIS

<u>Size Fraction</u>	<u>Weight Percent</u>	<u>Description</u>	<u>Phi Size</u>
18 x 35	0.22	Coarse Sand	0.0-1.0
35 x 120	86.39	Medium Sand Fine Sand	1.0-3.0
120 x 200	4.82	Very Fine Sand	3.0-3.7
200 x 325	4.18	Very Fine Sand Coarse Silt	3.7-4.5
-325	4.39	Coarse Silt and Finer	

TABLE 4. COMPUTER TEST CASES

<u>Input</u>	<u>Oxygen</u>	<u>20°C</u>	<u>55°C</u>	<u>100°C</u>	<u>150°C</u>
1) Supply Water Alone	-	-	X	X	X
2) Supply Water Alone	X	X	X	X	X
3) Storage Water Alone	-	X	X	X	X
4) Supply Water Plus Storage Water	X	X	X	X	X
5) Supply Water Plus Storage Water Plus Minerals	X	-	X	X	X

TABLE 5. MINERALS PRECIPITATED DUE TO HEAT, OXYGEN AND/OR FLUID-FLUID INCOMPATIBILITY

Fluid	Oxygen	Temperature (°C)	pH	Eh	Insoluble Minerals	Quantity (moles/kg water)
616	Yes	20	7.19	+0.807	quartz SiO_2 hematite Fe_2O_3	0.192E-03 0.627E-06
		55	8.36	+0.541	hematite Fe_2O_3	0.627E-06
		100	7.77	+0.354	hematite Fe_2O_3	0.627E-06
		150	7.34	+0.226	hematite Fe_2O_3	0.627E-06
	No	55	8.36	-0.215	minnesotaite $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	0.418E-06
		100	7.77	-0.159	hematite Fe_2O_3	0.627E-06
		150	7.34	-0.178	hematite Fe_2O_3	0.627E-06
	No	20	7.38	-0.091	quartz SiO_2 minnesotaite $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	0.274E-03 0.328E-06
		55	8.95	-0.268	minnesotaite $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	0.328E-06
		100	8.36	-0.196	hematite Fe_2O_3	0.492E-06
		150	7.90	-0.212	hematite Fe_2O_3	0.492E-06
	Yes	20	7.27	+0.367	quartz SiO_2 hematite Fe_2O_3	0.234E-03 0.560E-06
		55	8.76	-0.079	hematite Fe_2O_3	0.560E-06
		100	8.17	-0.120	hematite Fe_2O_3	0.560E-06
		150	7.71	-0.151	hematite Fe_2O_3	0.560E-06

TABLE 6. WATER AND MINERAL EQUILIBRIUM CONCENTRATIONS AT VARIOUS TEMPERATURES

Aqueous Species	Moles/kg H ₂ O			
	20°C	55°C	100°C	150°C
N ⁺	0.247-03	0.125-02	0.125-02	0.125-02
Ca ⁺⁺	0.611-05	0.614-04	0.284-03	0.601-03
Fe ⁺⁺	0.492-06	0.318-13	0.193-22	0.288-16
Fe ⁺⁺⁺	0.627-06	0.405-13	0.270-12	0.547-11
Si	0.316-03	0.291-03	0.845-03	0.215-02
CO ₃ ⁻	0.132-03	0.476-02	0.407-02	0.828-02
OH ⁻	0.100-06	-	-	-
H ⁺	0.100-05	-	-	-
O ₂	0.390-03	-	-	-
Al ⁺⁺⁺	-	0.124-05	0.203-05	0.720-05
K ⁺	-	0.690-03	0.234-02	0.233-02
pH	7.27	8.260	7.270	6.760
Eh	-	+0.018	+0.769	+0.361
P _{CO}	-	-	0.047	0.417
<u>Mineralogy</u>				
Calcite (CaCO ₃)	0.100-01	0.537-02	0.606-02	0.186-02
Quartz (SiO ₂)	0.400-02	0.609-02	0.505-02	0.751-02
Hematite (Fe ₂ O ₃)	0.100-02	0.100-02	0.100-02	0.100-02
Muscovite (KAl ₃ Si ₃ O ₁₀ (OH) ₂)	0.100-02	0.280-05	-	-
Kaolinite (Al ₄ Si ₄ O ₁₀ (OH) ₈)	0.100-02	0.707-03	-	-
Microcline (KAlSi ₃ O ₈)	0.100-02	-	-	-
Low Albite (NaAlSi ₃ O ₈)	0.100-02	-	-	-
k-Montmorillonite K _{0.7} (Al,Mg,Fe) ₄ (Al,Si) ₈ O ₂₀ (OH) ₄ · nH ₂ O	0.100-02	-	-	-
Adularia (KAlSi ₃ O ₈)	-	0.164-02	-	-
Zoisite (Ca ₂ Al ₃ Si ₃ O ₁₂ (OH))	-	0.228-02	0.160-02	0.377-02
Ca-Montmorillonite (1/2Ca) _{0.7} (Al,Mg,Fe) ₄ (Al,Si) ₈ O ₂₀ (OH) ₄ · nH ₂ O	-	-	0.280-02	-
Total	2.00-02	1.710-02	1.65-02	1.41-02

TABLE 7. POTENTIAL DAMAGE MECHANISMS FOR THE AUBURN FIELD TESTS

<u>Mechanism</u>	<u>Qualitative Potential</u>	<u>Comments</u>
<u>Temperature-Induced Phenomena</u>		
• Mineral precipitation	Low	Mathematical modeling potential for dissolved oxygen in the supply aquifer
• Outgassing	Moderate	
• Increased quartz-water boundary layer viscosity	Unknown	Limited available data
• Microstructural deformation	Unknown	Limited available data
<u>Fluid-Fluid and Fluid-Rock</u>		
<u>Chemical Incompatibility</u>		
• Clay swelling and dispersion	High	Significant montmorillonite, low salinity water injection
• Mineral precipitation (fluid mixing)	Low	Mathematical modeling
• Mineral precipitation (oxidation)	Low	Mathematical modeling
<u>Fluid-Rock Physical Incompatibility</u>		
• Suspended solids	Moderate	Potential for micron and sub-micron particles in the supply aquifer water
• Existing formation	High	Loose clay and silt particles

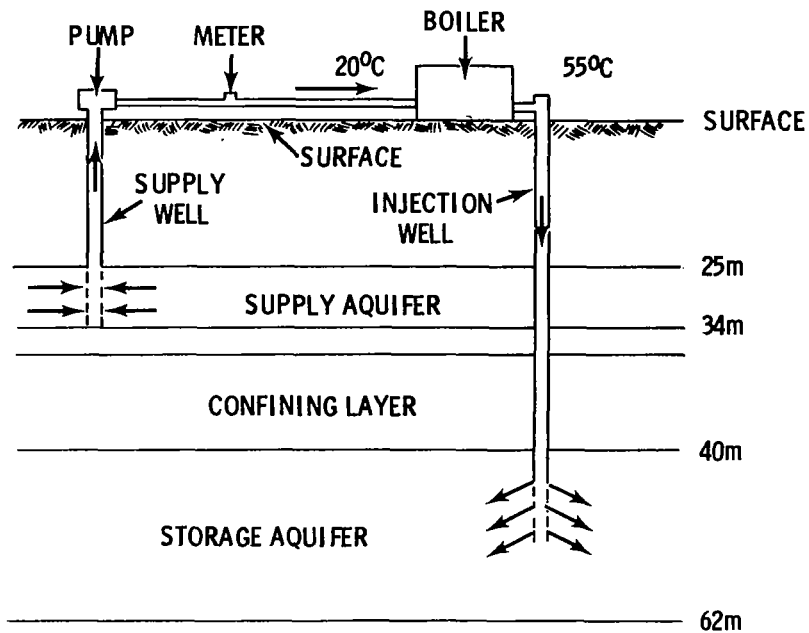
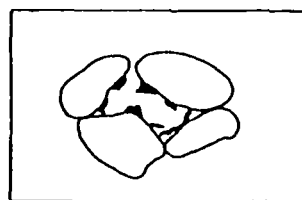


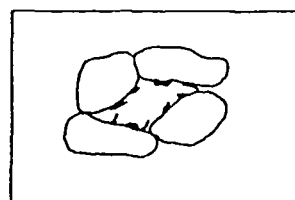
FIGURE 1. SCHEMATIC DIAGRAM OF THE SECOND MOBILE, ALABAMA, FIELD TEST SYSTEM (ref. 2)

SWELLING CLAY

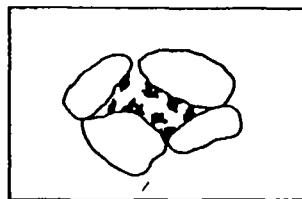
PARTICLE PLUGGING



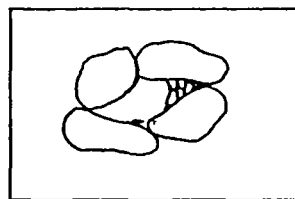
brine



brine



fresh water



fresh water

FIGURE 2. CONCEPTUALIZATION OF CLAY SWELLING AND DISPERSION